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Effect of Slag Composition on Inclusion Control in LF-VD Process for Ultra-low Oxygen Alloyed Structural Steel

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Abstract

Inclusion control in LF-VD process for ultra-low oxygen alloyed structural steel is investigated. It is found that after Al-deoxidation during tapping process, with slag of high basicity, high Al_2O_3 content and low oxidizing property, Al_2O_3 inclusions, which are the product of Al-deoxidation could transform to MgO-Al_2O_3 spinel, and later on to CaO-MgO-Al_2O_3 inclusions of lower melting point, which are inclined to be eliminated by floatation, thus total oxygen content would be lowered. On the other hand, residual inclusions in steel are mostly ultra-fine in size, and could be deformed slightly in hot-working process of steel, enhancing fatigue life of steel.

Key words: slag; inclusion; ultra-low oxygen; refining

1. Introduction

Alloyed structural steel suffers from recycling and alternative stress in its service life, leading to fatigue destruction, one of the main failing forms. Hard, brittle and un-deformable non-metallic inclusions are usually the origin of fatigue crack. Therefore, this kind of inclusions must be controlled properly in order to enhance fatigue performance of steel. As for Al-killed alloyed structural steel, the majority of inclusions at the beginning of refining are Al_2O_3 inclusions of high melting point, un-deformable, with edges and corners, causing clogging of nozzles, as well as ruining fatigue performance of steel.

Previous reports on inclusion control show that during refining process of ultra-low oxygen steel, with the decrease of total oxygen content, MgO-Al_2O_3 spinel would appear[1,2], which would be promoted by the increase of MgO, Al_2O_3, CaO/SiO_2, CaO/Al_2O_3 in slag[3-6]. However, SiO_2 in slag would suppress reduction of MgO, CaO in slag by [Al]s in steel, which is not beneficial for transformation of the product of Al deoxidation. Previous reports on calcium treatment show that calcium treatment would transform inclusions of high melting point to those of lower melting point, protecting nozzles from clogging.

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However, if calcium treatment is not controlled well, $CaO\text{-}Al_2O_3$ of high melting point and CaS inclusions would appear, also leading to clogging of nozzles[9-12]. In addition, when Si-Ca cored wire is fed into molten steel, it is easy to boil intensively, leading to reoxidation.

Technique of inclusion control by top slag is used for Al-killed steel, aiming to transform Al_2O_3 inclusions to $CaO\text{-}MgO\text{-}Al_2O_3$ inclusions of lower melting point, slightly deformable in hot-working process of steel, achieving ultra-low content of total oxygen and making inclusions' composition enter 1500℃ liquid zone of $CaO\text{-}MgO\text{-}Al_2O_3$ ternary phase diagram, enhancing fatigue performance of alloyed structural steel.

2. Experimental and Results

2.1. Experimental

Three furnaces are studied in plant. Production flow is LD → LF → VD → calcium treatment → soft bottom-blown by Ar bubbling → continuous casting. Calcium treatment is used in former two furnaces in order to make sure of smooth casting, while the third furnace is exempted from calcium treatment. With Al-deoxidation during tapping and top slag of high basicity, high Al_2O_3 content, and low oxidizing property, interaction of slag-steel-inclusion would happen, making inclusions' composition into 1500℃ liquid zone of $CaO\text{-}MgO\text{-}Al_2O_3$ ternary phase diagram. Steel and slag samples are fetched all through the whole process from beginning of LF to continuous casting. Concrete sampling points are beginning of LF, early stage of LF, middle stage of LF, late stage of LF, end point of LF, after VD, after calcium treatment, after soft bottom-blown by Ar bubbling, 30 and 60 tons of molten steel casted in tundish, 1/2 and 3/4 radius of round billet, abbreviated as LF1, LF2, LF3, LF4, LF5, VD1, VD2, VD3, CC1, CC2, 1/2R, 3/4R in following discussion. Number and size distribution of inclusions are studied by Leica optical microscope. Morphology and composition of inclusions are investigated by SEM-EDS. Chemical composition of steel and slag samples is analyzed at NACIS (National Analysis Center of Iron & Steel).

2.2. Results

2.2.1 Achievements of T[O] control

Table 1 shows average chemical composition of round billets in this experiment. It is shown by table 1 that averaged T[O] in billets is 0.0007%, symbolizing high cleanness of final product.

Table 1 Average chemical composition of round billets, %

C	Si	Mn	P	S	Als	Ca	Ti	Cr	T[O]	N
0.60	0.30	0.73	0.015	0.0017	0.029	0.0007	0.0056	0.18	0.0007	0.0034

Fig.1 shows changes of T[O] through the whole process. LF1 does not show data of NO.1 furnace because of failed sampling. VD2 only shows data of NO.1 furnace because of failed sampling of NO.2 furnace and exemption of NO.3 furnace from calcium treatment. It is shown by Fig.1 that T[O] increases before LF4 or LF5, after that it decreases. T[O] of NO.3 furnace at VD3 suddenly rises owing to reoxidation by sampling after breaking hard slag layer, not relevant to experimental process. It can also be seen from Fig.1 that from VD to continuous casting, T[O] stabilizes at the range of 0.0006~0.0009%, showing good shielded casting.

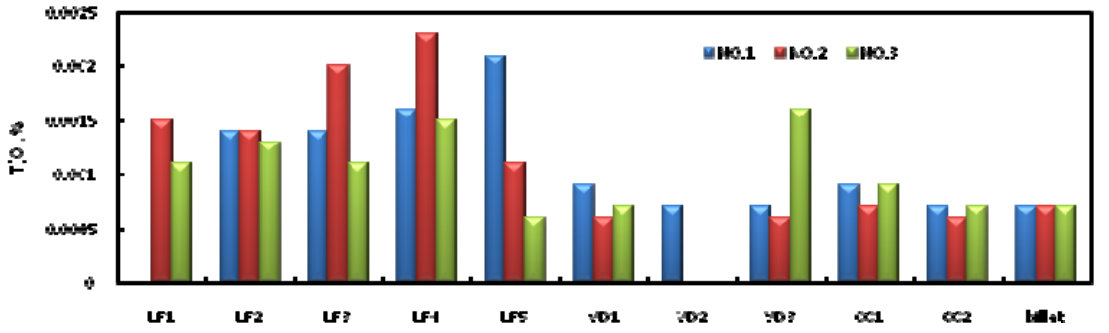


Fig.1 Changes of T[O] through the whole process, %

2.2.2 Achievements of inclusion control

Fig.2 shows changes of number of inclusions through the whole process. It is shown by Fig.2 that number of inclusions is inclined to decrease generally, and number of inclusions in round billet is lowered to 10~15/mm^2. Inclusions in LF-VD process are mainly considered, and calcium treatment is after VD, so composition changes of inclusions do not be discussed respectively between calcium-treated furnace and non-calcium-treated furnace.

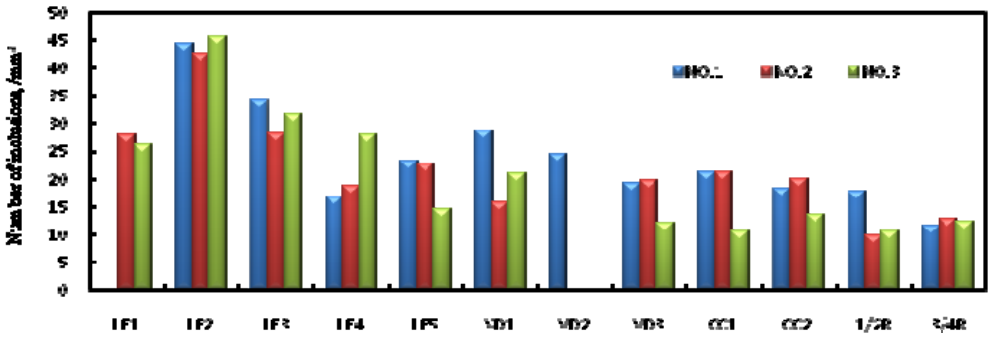


Fig.2 Changes of number of inclusions through the whole process, /mm^2

Fig.3 shows three kinds of oxide inclusions in refining process. Inclusions transform by sequence of a) → b) → c). Main inclusion at LF1 is Al_2O_3, which transforms to MgO-Al_2O_3 from LF1 to LF4, and some CaO-MgO-Al_2O_3 inclusions appear at this moment. After that, inclusions transform to CaO-MgO-Al_2O_3, and some MgO-Al_2O_3 inclusions still exist. CaO-MgO-Al_2O_3 takes up the majority of inclusions after LF process. Because [Ca] in steel would reduce MgO in MgO-Al_2O_3 inclusion from its outside, morphology of CaO-MgO-Al_2O_3 complex inclusion is cored structure, whose inside is MgO-Al_2O_3, outside is CaO-Al_2O_3 of lower melting point, reducing harm of MgO-Al_2O_3 spinel to steel performance.

Fig.4 shows line scan and element mapping of CaO-MgO-Al_2O_3 inclusion. It can be seen that MgO-Al_2O_3 spinel exists inside CaO-MgO-Al_2O_3 inclusion, cored by CaO-Al_2O_3.

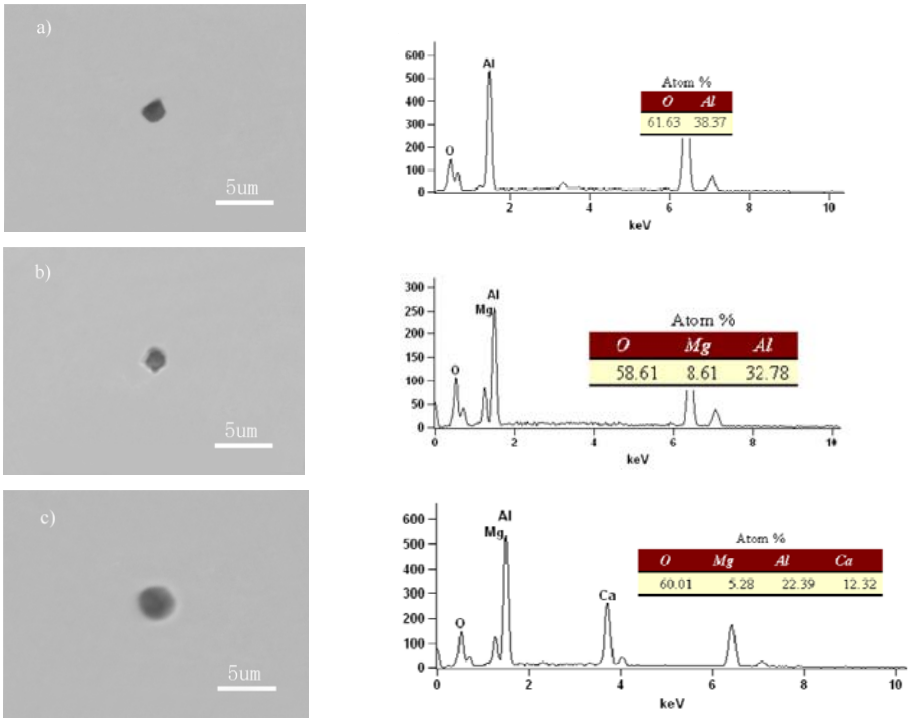
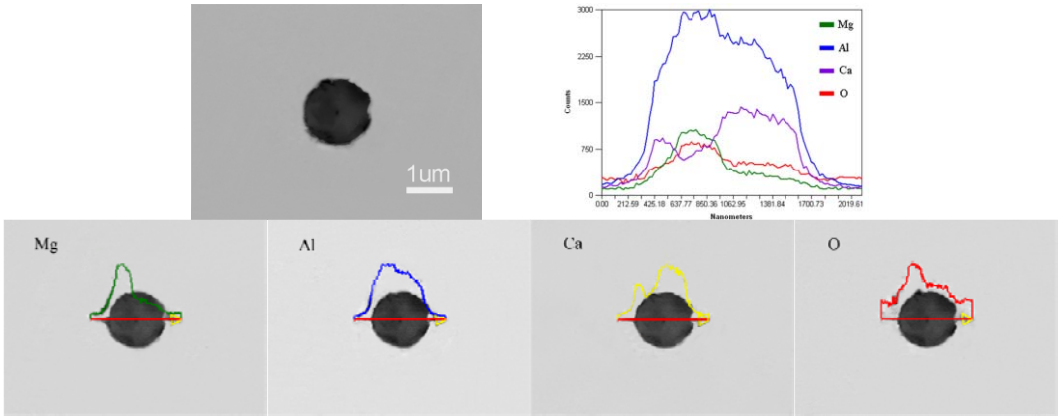
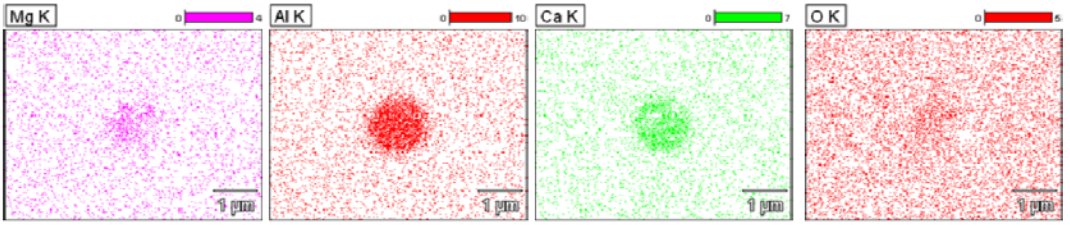


Fig.3 Three kinds of oxide inclusions in refining process a) Al_2O_3; b) MgO-Al_2O_3; c) CaO-MgO-Al_2O_3



a) Line scan



b) Mapping

Fig.4 Line scan and mapping of CaO-MgO-Al_2O_3 inclusion

3. Discussion

Inclusion control by top slag is realized by slag-steel interaction and steel-inclusion interaction. Following discussions are made according to this mechanism.

3.1. Slag-steel interaction

During LF process, [Mg], [Ca] in steel increases gradually, owing to slag-steel reactions shown as (1), (2), letting (MgO), (CaO) in slag be reduced by [Al]s in steel. The other source of MgO is furnace lining.

$$2[Al]s+3(MgO)=3[Mg]+(Al_2O_3) \quad (1)$$

$$2[Al]s+3(CaO)=3[Ca]+(Al_2O_3) \quad (2)$$

Fig.5 shows changes of (CaO), (MgO), (Al_2O_3) in slag. It is shown by Fig.5 that (CaO) stabilizes at about 50% in LF process, then declines to 42% after VD. This is because refining slag is added several times during LF process, resuming (CaO) in slag consumed on reduction by [Al]s in steel. (MgO) keeps general rising trend in LF-VD process from 5.7~10%. (MgO) is supposed to decline if the reaction shown as (1) is only considered, but actual data rises because MgO in furnace lining enters slag, and added refining slag contains MgO. (Al_2O_3) shows slight rising trend in LF process, then rises suddenly to 39% after VD as a result of three factors: (i)Al particles are added into slag for diffusion deoxidation; (ii) Al_2O_3, product of the reactions shown as (1), (2) enters slag; (iii)inclusions are absorbed by slag.

Fig.6 shows changes of [Ca], [Mg], [Al]s in steel. If the reactions shown as (1), (2) are only considered, [Al]s is supposed to decline. However, it is shown by Fig.6 that [Al]s rises to 0.084% at LF3, then declines to 0.018% at VD1, because Al particles are added into slag for diffusion oxidation in early stage of LF process, leading to the increase of [Al]s in steel, much more than the amount of [Al]s oxidized by (MgO), (CaO) in slag. [Mg], [Ca] in steel rises to 0.0007% and 0.0012% respectively at LF4, because the product of reduction of (MgO), (CaO) by [Al]s enters molten steel. After LF4, [Mg], [Ca] in steel declines to 0.0005% and 0.0008% respectively at VD1 because of vaporization and reaction with inclusions.

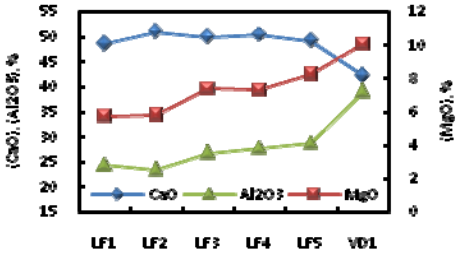


Fig.5 Changes of (CaO), (MgO), (Al_2O_3) in slag

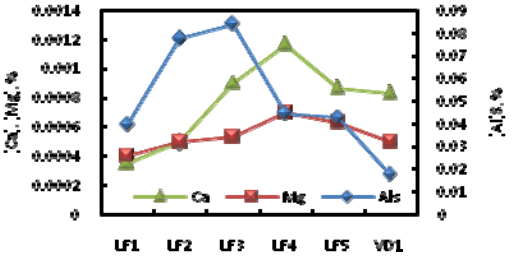


Fig.6 Changes of [Ca], [Mg], [Al]s in steel

Fig. 7 shows effect of slag basicity on [Mg], [Ca] in steel. It is shown by Fig.7 that [Mg], [Ca] in steel increases as slag basicity increases. When R is about 10, [Mg], [Ca] in steel is 0.0006% and 0.0011%

respectively. It can be deduced that high basicity slag would promote the reactions shown as (1), (2), however which are suppressed by (SiO_2) in slag, keeping good accordance to references[7, 8].

Fig.8 shows effect of (FeO+MnO) in slag on [Mg], [Ca] in steel. It is shown by Fig.8 that [Mg], [Ca] in steel increases as (FeO+MnO) in slag decreases. When (FeO+MnO) in slag is 0.9%, [Mg], [Ca] in steel is 0.0007% and 0.0011% respectively. It can be deduced that slag with low oxidizing property promotes the reactions shown as (1), (2).

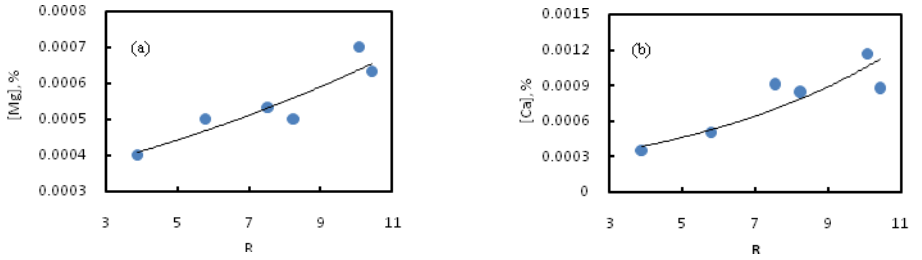


Fig.7 Effect of slag basicity on (a) [Mg], (b) [Ca] in steel

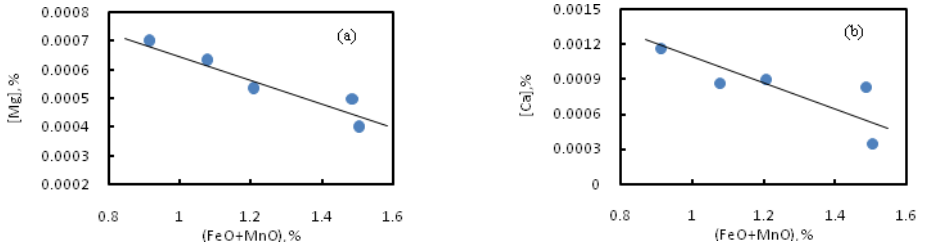


Fig.8 Effect of (FeO+MnO) in slag on (a) [Mg], (b) [Ca] in steel

3.2. Steel-inclusion interaction

With increase of [Mg], [Ca] in steel, steel-inclusion interaction would happen, shown as (3), (4), transforming Al_2O_3 gradually to MgO-Al_2O_3, then to CaO-MgO-Al_2O_3 complex inclusions with lower melting point.

$$3[Mg]+n(Al_2O_3)_{inclusion}=(3MgO\cdot(n-1)\ Al_2O_3)_{inclusion}+2[Al] \quad (3)$$

$$x[Ca]+[yMgO\cdot zAl_2O_3]_{inclusion}=[xCaO\cdot(y-x)MgO\cdot zAl_2O_3]_{inclusion}+x[Mg] \quad (4)$$

With high basicity slag, Mg reduced from MgO by [Al]s enters molten steel. So it is inevitable for the formation of MgO-Al_2O_3 spinel, which was also proven in references[1, 2]. Nevertheless, if the reaction shown as (4) performs fully, there would be an adequately thick layer of CaO-Al_2O_3 of lower melting point outside MgO-Al_2O_3, whose harm would be reduced.

Fig.9 shows changes of average composition proportion in inclusions. It is shown by Fig.9 that with the progress of refining, proportion of Al_2O_3 in inclusions decreases gradually from 97.8% at LF1 to 62.7% at LF4, then increases slightly to 66.9% at VD1. Proportion of MgO in inclusions increases from 1.6% at LF1 to 13.5% at LF4, then decreases to 7.8% at VD1. Proportion of CaO in inclusions increases from 0.6% at LF1 to 25.2% at VD1, a little bit later than the increase of the proportion of MgO, owing to the sequent progress of reactions shown as (3), (4). Before LF4, Al_2O_3 inclusion transforms to MgO-Al_2O_3, raising the proportion of MgO in inclusions. The transformation of MgO-Al_2O_3 to CaO-MgO-Al_2O_3 happens a little bit later than the transformation of Al_2O_3 to MgO-Al_2O_3, but it plays the major role after LF4, raising the proportion of CaO in inclusions, and reducing the proportion of MgO in inclusions because of the reduction of MgO in inclusions by [Ca] in steel.

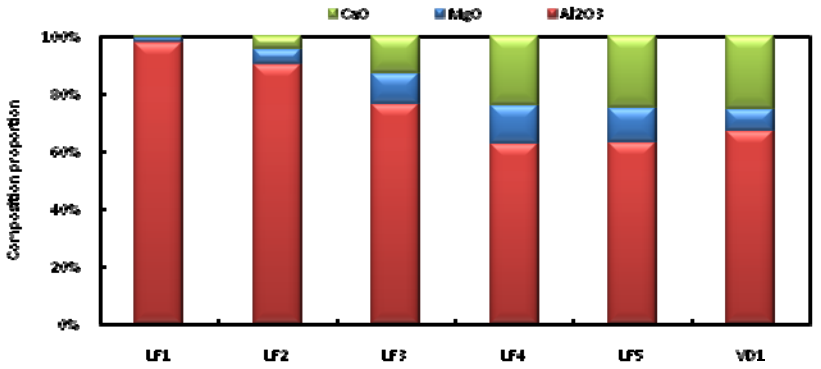


Fig.9 Changes of average composition proportion in inclusions

Fig.10 shows effect of [Mg] in steel on MgO in inclusions and Fig.11 shows effect of [Ca] in steel on CaO in inclusions. It is shown by Fig.10 that MgO in inclusions increases as [Mg] in steel increases, and by Fig.11 that CaO in inclusions increases as [Ca] in steel increases. When [Mg] content in steel is 0.0007%, MgO content in inclusions is 10.5%. When [Ca] content in steel is 0.0009~0.0012%, CaO content in inclusions is 16.7~21.4%. It can be deduced that [Mg], [Ca] in steel respectively promotes the reactions shown as (3), (4).

Extent of reactions shown as (3), (4) can be described by MgO/Al_2O_3 and CaO/MgO respectively. Fig.12 shows effect of [Mg] in steel on MgO/Al_2O_3 in inclusions. Fig.13 shows effect of [Ca] in steel on CaO/MgO in inclusions. It is shown by Fig.12 that MgO/Al_2O_3 in inclusions increases as [Mg] in steel increases, and by Fig.13 that CaO/MgO in inclusions increases as [Ca] in steel increases. When [Mg] content in steel is 0.0007%, MgO/Al_2O_3 in inclusions is 0.22. When [Ca] content in steel is 0.0009~0.0012%, CaO/MgO in inclusions is 1.76~2.

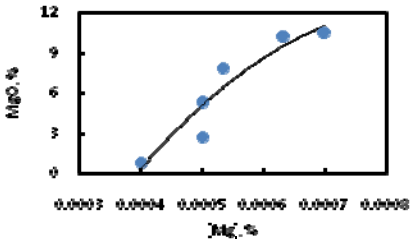


Fig.10 Effect of [Mg] in steel on MgO in inclusions

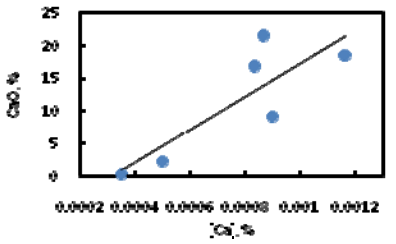


Fig.11 Effect of [Ca] in steel on CaO in inclusions

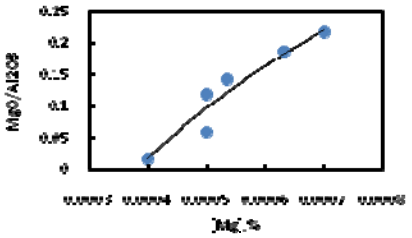


Fig.12 Effect of [Mg] in steel on MgO/Al_2O_3 in inclusions

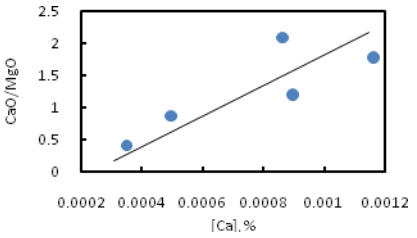


Fig.13 Effect of [Ca] in steel on CaO/MgO in inclusions

Fig.14 shows inclusion transformation route in LF-VD process by projecting average composition of all inclusions at every sampling point in LF-VD process (LF1~VD1) to ternary phase diagram of CaO-MgO-Al_2O_3. The blue shaded area symbolizes 1500℃ liquid zone, which is the target zone for inclusion control. It is shown by Fig.14 that the majority of inclusions are Al_2O_3 at the beginning of LF. With the progress of refining, spots of inclusions' composition close to 1500℃ liquid zone gradually, and begin to enter this zone since late stage of LF, although not completely. Inclusion transformation is a persistent and time-consuming process of slag-steel-inclusion interaction bounding to equilibrium. However, time of LF-VD process is not adequate for complete inclusion transformation. But fortunately, there is plenty of time for inclusions to continue to transform from the end point of VD to solidification of molten steel. In the end, most inclusions' composition would enter 1500℃ liquid zone.

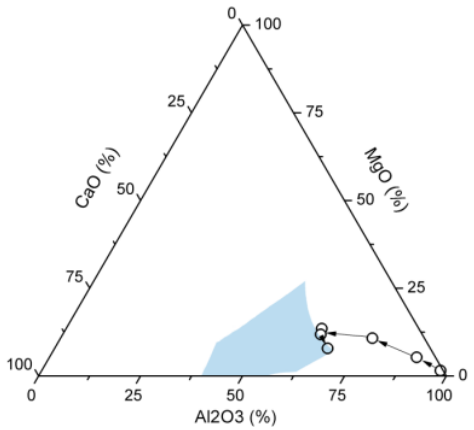


Fig.14 Inclusion transformation routine in LF-VD process

4. Conclusions

Under the condition of Al deoxidation and slag of high basicity, high Al_2O_3 content and low oxidizing property, effect of slag composition on inclusion control in LF-VD process for ultra-low oxygen alloyed structural steel is investigated. Conclusions are drawn as below.

1) On one hand, low content of soluble oxygen is achieved by Al-deoxidation. On the other hand, most liquid inclusions would be eliminated by floatation. Both would lower the content of T[O] to 0.0007% in round billets, achieving high cleanness of steel;

2) Slag composition is controlled well in LF process, which would be beneficial to get proper composition of molten steel to promote the transformation of Al_2O_3→MgO-Al_2O_3→CaO-MgO-Al_2O_3. Most inclusions' composition would begin to enter 1500℃ liquid zone from late stage of LF process, owing to proper composition of molten steel, which is beneficial for inclusions to continue to transform and to be eliminated by floatation until solidification of molten steel;

3) Number of inclusions decreases apparently owing to agglomeration and floatation. Inevitably residual inclusions in steel are spherical or spherical-alike inclusions with ultra-fine size, lower melting point and slight deformability in hot-working process of steel.

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